## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventors: Brian S. Appel et al.

Serial No.: 10/717,076

Filed: November 18, 2003

Title: Process For Conversion of Organic, Waste, Or Low-Value Materials Into Useful Products

Examiner: Tam M. Nguyen

Attorney Docket No.: 12833-011USU1

Confirmation No.: 6999

Commissioner for Patents
Alexandria, VA 22313-1450

## Declaration of James H. Freiss, P.E. under Rule 132

I, James H. Freiss, declare as follows:

1. I am the Chief Operating Officer at Changing World Technologies, Inc. the exclusive licensee of the present application. I am also a named inventor on the present application.

2. I have a Bachelor of Science degree in Agricultural Engineering from Penn State University and I am a licensed Professional Engineer in the state of Delaware. Prior to assuming my current position I had over twenty years of environmental and waste management engineering experience with a number of different agricultural, food processing related positions. I am also the inventor on two issued patents and four pending US patent applications in addition to the present application. Each of these additional patents and applications relates to aspects of waste processing and conversion of wastes in to useful materials.

3. I am familiar with the contents of the present application. I have read and understood the office actions and prior art cited by the Examiner. In particular, I have read and understood the office action dated April 17, 2010 and the patent to Lang that the Examiner uses as the basis for the rejections.

4. Based on my experience in the art and my familiarity with the present application, it is my opinion that a person of ordinary skill in the art as related to the present invention would be a person with at least a bachelor's degree in a process engineering related field such as chemical engineering or agricultural engineering and at least a number of years of intensive experience with waste and food processing related systems.

5. As a person of at least ordinary skill in the art, I disagree with the Examiner that the claimed process is obvious in light of the Lang patent. Fundamentally, the process disclosed by Lang is a biologically based process that differs dramatically from the physical/chemical process of the present invention. For this reason alone, a person of ordinary skill in the art would not turn to Lang to develop or improve processes for the production of hydrocarbons, in particular oil, from the wide variety of feedstocks suitable for use with the present invention. A person of ordinary skill in the art would thus have no reason to modify Lang to achieve the process conditions and results of the present invention.

6. Lang discloses a process of making an ethanol fuel from a solid municipal waste feed by fermentation. Such processes are numerous and well understood in the art. In order to produce "fermentable sugar-like materials" by saccharification through hydrolysis, Lang first teaches a series of flotation based separation steps to produce what is referred to as "hydrolzable materials." (Col. 2, lns. 5-37). The hydrolysis step is explained by Lang to be a step in which "hydrolyzables are saccharified to fermentable sugar-like materials." Based on this explanation and the general knowledge in the art regarding such processes, a person of ordinary skill in the art would understand Lang as teaching that its primary product of hydrolysis is a water stream containing dissolved short chain sugar compounds such as glucose suitable for fermentation to produce alcohol.

7. There is no specific, or even general, description of the hydrolysis conditions or process. This is likely because such hydrolysis processes to saccharafy a wide variety of feedstocks to produce dissolved short chain sugar compounds for fermentation are well understood in the art

8. In order to ensure that only the so-called "fermentable sugar-like materials," in other words dissolved short chain sugar compounds such as glucose, are delivered to the fermentation step, Lang employs post hydrolysis filtration and evaporation at steps 20 and 21. The materials removed in these steps are recycled back to hydrolysis. Fermentation (step 22) and the downstream processing steps as disclosed in Lang are again conventional steps in the production of alcohol based fuels such as ethanol, and are well known and understood in the art when applied to ethanol production as disclosed by Lang.

9. The Examiner asserts on page 6 of the Office Action that it would have been obvious to modify "the process of Lang by converting the liquid product to hydrocarbon oils as claimed." I disagree with this assertion. It is unclear as to what the Examiner is referring to. If the Examiner is referring to the liquid product of the Lang hydrolysis, then he is not correct because the product of hydrolysis in Lang is exclusively intended for fermentation. Converting it to a hydrocarbon oil would destroy its effectiveness for fermentation and thus destroy the intended purpose of the process disclosed in Lang. If instead the Examiner is referring to the final liquid fuel product of Lang (at step 28), he is also not correct because that product is an ethanol-water mixture, which cannot be converted to a hydrocarbon fuel oil.

10. The Examiner says that it would have been obvious to modify the operating parameters of Lang to meet the pressures and temperatures of the present invention as recited in the claims. He also says that a person skilled in the art would expect heating of the feedstock to improve the effectiveness of the reaction in Lang. I disagree with both of these statements. For a number of reasons. First, there are no particular process conditions described in Lang for the hydrolysis reaction. This is most likely because such hydrolysis reactions for the purpose of producing a fermentable feed are numerous and well known in the art. There is virtually an unlimited combination of process conditions that may be employed to achieve what Lang achieves, each with pros and cons related o particular applications. Given this wide variety of known choices, there is no reason for a person of ordinary skill to favor any one set of conditions over another absent a stated preference.

11. Among the many different types of hydrolysis reactions are reactions sometimes referred to as low temperature, low pressure reactions. Frequently such reactions involve a dilute acid catalyst. Typical examples of such processes are described in Farina et al., Fuel Alcohol Production From Lignocellulosic Feedstocks, Energy Sources, Vol. 10, 231-237 (1988), and Rocha et al., Enzymatic Hydrolysis and Fermentation of Pretreated Cashew Apple Bagasse with Alkali and Diluted Sulfuric Acid for Bioethanol Production, Applied Biochem and Biotech, vol. 155, No. 1-3, May 2009, pp. 104-114 (hydrolysis at 45°C). The Farina article describes a two-stage, low-temperature, ambient pressure, acid hydrolysis process for converting feedstocks containing cellulose to fermentable sugars. The hydrolysis temperature described in this article is 100 °C at ambient pressure. The Rocha article describes a hydrolysis temperate of only 45 °C. Copies of these articles are included.

12. Given the lack of specific process parameters for hydrolysis in Lang, a person of ordinary skill in the art would be directed to low pressure, low temperature dilute acid hydrolysis for a number of reasons. First, Lang distinguishes his invention from high pressure and temperature processes by describing disadvantages of such processes, including high capital investment. Thus, use of specialized reactor vessels capable of withstanding high pressures and temperatures is taught away from by Lang. Second, Lang describes the use of Sulfurous acid as a hydrolysis catalyst in his example. A person of ordinary skill in the art would understand this to be a dilute acid process. This combined with the teachings away from high temperature and pressure clearly leads a person of ordinary skill in the art to understand that Lang intended to employ a low temperature, low pressure dilute acid hydrolysis process.

13. Given the existence of the low temperature and low pressure dilute acid hydrolysis processes as mentioned above, there would have been no expectation by a person skilled in the art that the hydrolysis in Lang would be at or above the saturation pressure as stated by the Examiner. For example, the process described by the Farina article mentioned above is operated at 100 °C and ambient pressure. It is well known that the boiling point of water at ambient pressure is 100 ° C. Thus, operation at these conditions

would not be expected to and would not maintain the pressure above the saturation pressure because it would permit water to boil off.

14. The Examiner also says that Lang would produce a small amount of oil and cites to a number of locations in the patent, which amounts to almost the entire disclosure. I have studied the Lang patent in detail and can find no reference whatsoever to the production of oil in any of the passages cited by the Examiner. This is not surprising because if Lang is using low temperature, low pressure dilute acid hydrolysis as is most likely based on the information provided, oil generally would not result from the hydrolysis step described.

15. But even if the process as described by Lang did somehow produce oil in its hydrolysis step, the post-hydrolysis processing steps described in the claims of the present application are not disclosed in Lang. It also would not have been obvious to a person of ordinary skill in the art to modify the Lang process to meet those steps as claimed. The hydrolysis reaction of the present invention produces a number of products, including reacted solids, and reacted liquids. The reacted liquids generally include produced water, which contains soluble, and a liquid mixture of carbon-containing species. Depending on feedstocks employed, this liquid mixture may be comprised of floatable organic materials.

16. The products of hydrolysis in Lang are filtered and evaporated to concentrate the "fermentable sugar-like materials" into a filtrate that is directed to the fermentation step. It would be well understood by persons of ordinary skill in the art that such a filtrate would consist primarily of water with dissolved short chain sugar compounds such as glucose. Thus, to the extent that the process of Lang might be compared to the present invention, this Lang filtrate could be said correspond to the produced water of the present invention in that both are water containing solubles including dissolved short chain sugar compounds.

17. But the treatment of the produced water in the present invention is dramatically different from the treatment of the filtrate in Lang. For example, claim 1 of the present application states that the further processing step of converting to form a useful material is a

conversion of the liquid mixture of carbon-containing species, not the produced water. Instead, Lang specifically describes recycling the products of hydrolysis other than the filtrate to direct them back into hydrolysis. (See Fig. 1, Residue Recycle and Catalyst Recycle lines.). A person of ordinary skill in the art would not modify Lang to meet the claim language because the process would then not work for fermentation.

18. Other specific claim limitations in the claims of the present application are also not disclosed or taught in Lang. For example, the present application describes the removal of free ammonia, especially when the feedstock comprises animal processing wastes (Paragraph [0083]). This removal may separate animal urine prior to slurrying, the use of enzymatic degradation, application of heat or conversion to salt by acidification. No such processes are suggested or disclosed by Lang. A person of ordinary skill in the art also would not add such processing steps because the reactions that take place in the Lang process are dramatically different than those of the claimed invention.

19. In another example of the lack of correspondence between the claims of the present application and Lang, claims 18 and 19 recite diverting a portion of the reacted liquid product prior to the converting step and then converting that diverted portion into a specialty chemical, such as a fatty acid. No such steps or products are disclosed or suggested in Lang. There is no diversion of any product of the hydrolysis prior to fermentation except back into the hydrolysis. There is also no reason for a person of ordinary skill in the art to add such a step at that point because the process of producing fermentable materials so different from the present invention that there would be no expectation of achieving a benefit by such a modification.

20. Another difference between Lang and the present invention is the liquid/liquid separation described in paragraph [0164] and shown in FIG. 8A. Here the converting step is described as comprising a liquid/liquid separation performed on the liquid mixture of carbon-containing species that makes up a part of the reacted liquid product from the hydrolysis reaction. An oil is produced for sale as a final product by these steps. Lang does not disclose or suggest production of a fuel <u>oil</u> as described. There is no liquid mixture of carbon containing species produced in the Lang hydrolysis and even if there

were, there is simply no liquid/liquid separation disclosed in Lang that can correspond to these processing steps. These steps are recited for example in claims 87 and 88 of the present application.

21. Another area of difference with Lang is the use of decomposition and hydrolysis reactions, reactions that at least in part deaminate and decarboxylate the feedstock. These specific steps, which are not suggested in Lang, are described, for example, in the present application at paragraphs [0060-61] and [0087]. Nothing in the Examiner's comments indicates that he has addressed these aspects of the present invention, which appear for example in Claims 93-95, and 108. It is not surprising that Lang does not disclose such reactions. The objective of the Lang process is to produce a fermentable material; such reactions are not necessary and there would be no reason for a person of ordinary skill in the art to attempt to control the Lang process to produce such reactions. Also, because Lang seeks to avoid high temperatures and pressures as explained above, a person of ordinary skill in the art would not expect decomposition reactions as described in the present invention to occur or be useful in Lang.

22. Independent claims 75, 96 and 127 also contain limitations that distinguish those claims from Lang in a manner that a person of ordinary skill in the art would not be motivated to modify Lang. For example, among other things, claim 75 recites that the products of the reacting include a reacted liquid product that is made up of at least two components, floatable organic materials and water containing solubles. The way these materials are processed and separated after their formation is fundamentally different from the Lang process.

23. As another example of differences from Lang, claim 96 recites three different separations to obtain the claimed fuel oil. The first separating step separates liquid, gaseous and solid fractions produced in the reactions. There is no separation of a gaseous fraction disclosed at this point in the Lang process, which would be expected for a low temperature/pressure operation as described. Claim 96 then recites a second separating of water from the liquid fraction to produce a fuel oil containing liquid. While Lang does disclose downstream water removal after the fermentation, the product is ethanol, not a

fuel oil. The fuel oil containing liquid of the present invention is then subjected to a further separation of liquid to provide a fuel oil. This sequence of separation steps leading to provision of a fuel oil is not something that is taught or suggested to a person of ordinary skill in the art by the Lang patent.

24. The heating and reacting steps of claim 127 are different from Lang for reasons as explained above. After the reacting step, claim 127 recites a further sequence of steps that includes lowering the temperature and pressure of the reacted feed to produce an intermediate feed, separating the reacted solid product from the intermediate feed to produce a liquid mixture comprising organic liquor and produced water, separating said produced water from the organic liquor, and subjecting said organic liquor to a liquid-liquid separation to produce at least an oil fraction. The organic liquor is clearly described in the present application (paragraph [0064]) as a liquid that contains carbon-containing species. This specific sequence of steps and handling of the reaction products is not disclosed or suggested in Lang, nor would it be obvious to modify Lang to meet these limitations because Lang is concerned with producing ethanol via fermentation, not hydrocarbon oils.

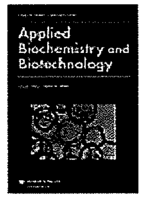
25. For all of the above reasons, it is my opinion as a person of skill in the art that the Lang patent cited by the Examiner does not render the claims of the present application obvious because it does not disclose all of the claim limitations and would not be modified by a person of ordinary skill in the art to meet those limitations.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of Declarant: James H. Freiss, P.E.

Signature: ______________________ Date: October 18, 2010

# Enzymatic Hydrolysis and Fermentation of Pretreated Cashew Apple Bagasse with Alkali and Diluted Sulfuric Acid for Bioethanol Production

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**Source:** Applied Biochemistry and Biotechnology, Volume 155, Numbers 1-3, May 2009 , pp. 104-114(11)
**Publisher:** Humana Press

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**Abstract:**

The aim of this work was to optimize the enzymatic hydrolysis of the cellulose fraction of cashew apple bagasse (CAB) after diluted acid (CAB-H) and alkali pretreatment (CAB-OH), and to evaluate its fermentation to ethanol using *Saccharomyces cerevisiae*. Glucose conversion of 82 ± 2 mg/g CAB-H and 730 ± 20 mg/g CAB-OH was obtained when 2% (*w/v*) of solid and 30 FPU/g bagasse was used during hydrolysis at 45 °C, 2-fold higher than when using 15 FPU/g bagasse, 44 ± 2 mg/g CAB-H, and 450 ± 50 mg/g CAB-OH, respectively. Ethanol concentration and productivity, achieved after 6 h of fermentation, were 20.0 ± 0.2 g $L^{-1}$ and 3.33 g $L^{-1}$ $h^{-1}$, respectively, when using CAB-OH hydrolyzate (initial glucose concentration of 52.4 g $L^{-1}$). For CAB-H hydrolyzate (initial glucose concentration of 17.4 g $L^{-1}$), ethanol concentration and productivity were 8.2 ± 0.1 g $L^{-1}$ and 2.7 g $L^{-1}$ $h^{-1}$ in 3 h, respectively. Hydrolyzates fermentation resulted in an ethanol yield of 0.38 and 0.47 g/g glucose with pretreated CAB-OH and CAB-H, respectively. Ethanol concentration and productivity, obtained using CAB-OH hydrolyzate, were close to the values obtained in the conventional ethanol fermentation of cashew apple juice or sugar cane juice.

**Keywords:** Ethanol; Cashew apple bagasse; Pretreatment diluted acid sulfuric; Enzymatic hydrolysis; Saccharomyces cerevesiae; Cellulase
**Document Type:** Research article
**DOI:** 10.1007/s12010-008-8432-8

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*Energy Sources*, Volume 10, 231–237
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# Fuel Alcohol Production from Agricultural Lignocellulosic Feedstocks

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**Abstract** *A two-stage, low-temperature, ambient pressure, acid hydrolysis process that utilizes separate unit operations to convert hemicellulose and cellulose in agricultural residues and crops to fermentable sugars is being developed and tested by the Tennessee Valley Authority and the U.S. Department of Energy (DOE) in Muscle Shoals, Alabama. In laboratory and bench-scale evaluations, the conversion and recovery efficiencies of sugars from hemicellulose and cellulose fractions of corn stover were greater than 90%. Sugar product concentrations of more than 10% glucose and 10% xylose were achieved. In these tests, furfural and hydroxymethyl furfural levels in the sugar solutions never exceeded 0.02g/100 mL, which is far below the levels shown to inhibit fermentation. Based on the results of the bench-scale tests, TVA built a one-of-a-kind acid hydrolysis experimental plant to demonstrate the concepts of low-temperature acid hydrolysis on a much larger scale. The experimental plant was coupled to an existing 10 gal/h fermentation and distillation facility. Plant tests using corn stover have been conducted for more than a year and conversion efficiences have equaled those achieved in the laboratory. Laboratory tests to determine the potential for low-temperature acid hydrolysis of other feedstocks—including red clover, alfalfa, kobe lespedeza, winter rape, and rye grass—are being conducted. Where applicable, process modifications to include extraction before or after hydrolysis also are being studied. This paper describes the experimental plant and process, results obtained in the plant, results of alternative feedstocks testing in the laboratory, and a plan for an integrated system that will produce other fuels, feed, and food from crops grown on marginal land.*

Process technology for producing fermentable sugars from agricultural crops and residues is being developed and tested by the Tennessee Valley Authority (TVA) in conjunction with the Solar Energy Research Institute (SERI) and the U.S. Department of Energy (DOE) at the TVA research center in Muscle Shoals, Alabama. A two-stage, low-temperature, low-pressure sulfuric acid hydrolysis process experimental plant designed to convert the carbohydrates hemicellulose and cellulose in corn stover to reducing sugars was built in 1984. The acid hydrolysis plant provides fermentable sugars to a 38-L/h fermentation and distillation facility built in 1980. Objectives of the project include (1) conducting experimental plant evaluations and laboratory tests to develop low-temperature acid hydrolysis process procedures; (2) defining technology, production systems, and feedstocks required for an integrated ethanol production system; and (3) identifying technology required for economical treatment, use, or disposal of process effluent streams.

Bench- and laboratory-scale process studies are conducted to define and evaluate potential process improvements before plant-scale testing. Work is now focused on developing an acid recovery process, using $C_5$ sugars, stillage, and other waste streams,

and reducing process and materials handling steps. The experimental plant is used to develop, test, and evaluate larger scale process systems, materials of construction, and materials handling systems. Based on experimental plant studies, optimum process conditions and equipment are being defined. Initial testing of the process has been completed. All process steps have been evaluated, and conversion efficiencies are greater than 90% for both hemicellulose and cellulose components of corn stover feedstock. Bench-scale and laboratory testing is also progressing well. Preliminary laboratory testing of a system to recover and recycle sulfuric acid is underway. Several studies to simplify the acid hydrolysis process are being evaluated. Some of these tests are conducted under contract for TVA at Mississippi State University (MSU) while others are conducted in-house by TVA staff.

## Process Background

TVA's process is based on the sulfuric acid hydrolysis process developed by Dunning and Lathrop (1945, 1948; U.S. Department of the Interior 1951) at the USDA Peoria Laboratory. Several variations of the Peoria process were evaluated at Purdue University's Laboratory of Renewable Resources Engineering (Ladisch 1983; Tsao et al. 1982) and other universities (Arkansas and Missouri). These studies were not sufficiently detailed to allow scaleup to the 38-L/h production level of TVA's experimental plant; therefore, experiments were conducted in TVA, vendor, and Mississippi State University laboratories to verify operating conditions, equipment requirements, and design parameters. Results of these studies are summarized below.

- Corn stover ground to 2.5 cm allowed adequate hydrolysis of hemicellulose.
- The time required for optimum hemicellulose hydrolysis in 10% acid at 100 °C was about 2 h.
- Overall xylose yields at 86 and 93% were obtained in bench-scale studies at 1- and 3-h reaction times, respectively.
- Recycled leachate, dilute acid, and prehydrolysis acid solutions were stable during storate for several days.
- Vacuum drying was adequate for the acid concentration drying step.
- Cellulose hydrolysis was successfully accomplished by cooking stover containing 66 to 78% acid for 6 h at 100 °C. Yields of 75 to 99% cellulose conversion to glucose were obtained in laboratory studies.
- Vinyl ester resin fiberglass reinforced plastics were adequate for construction of process vessels and piping.

## Process Description

The process involves two-stage sulfuric acid hydrolysis, relatively low temperatures, and a cellulose prehydrolysis treatment with concentrated acid. Shown in Figure 1 is a flow diagram of the TVA process. Corn stover is ground and mixed with dilute sulfuric acid (about 10% by weight). The hemicellulose fraction of the stover is converted to pentose sugars by heating the mixture to 100 °C for 2 h in the first hydrolysis reactor. Raw corn stover contains, on a dry basis, about 40% cellulose, 25% hemicellulose, and 25% lignin. Sulfuric acid for the first hydrolysis reaction is provided by recycling the product stream from the second hydrolysis step which contains sulfuric acid and hexose sugars.

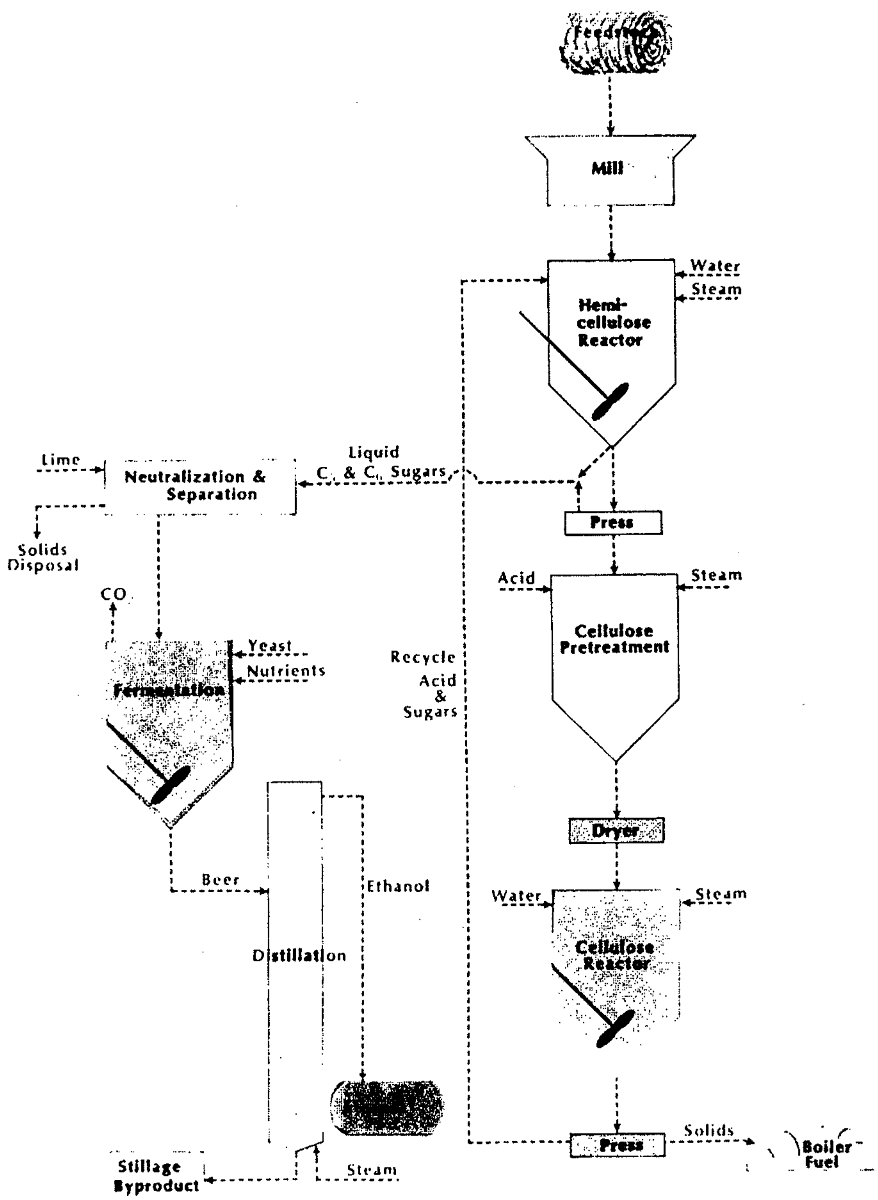


**Figure 1.** Low-temperature, low-pressure, two-stage, acid hydrolysis concept for conversion of nonwoody feedstocks to ethanol.

The pentose and hexose sugars, which are primarily xylose and glucose, respectively, are leached from the reactor with warm water. The sugar-rich leachate is then neutralized with lime, filtered to remove precipitated material, and fermented to produce ethanol.

Residue stover from the first hydrolysis reaction (hemicellulose conversion) is dewatered and prepared for the second hydrolysis step (cellulose conversion) by soaking (prehydrolysis treatment step) in sulfuric acid (about 20 to 30% concentration) from 1 to 2 h. The residue is then screened, mechanically dewatered, and vacuum dried to increase the

sulfuric acid concentration to 75 to 80% in the liquid phase before entering the cellulose reactor. The second hydrolysis reactor operates at 100 °C and requires a reaction time of 4 h. Acid concentration and reaction time are based on laboratory data shown in Figure 2. The reactor product is filtered to remove solids (primarily lignin and unreacted cellulose). Since the second hydrolysis reactor product stream contains about 10% sulfuric acid, it is used in the first hydrolysis step to supply the acid required for hemicellulose hydrolysis. Residue from the reactor is washed to recover remaining sulfuric acid and sugar not removed in the filtration step.

Fermentation organisms are being evaluated in other TVA studies to convert the xylose component of the sugar solution to ethanol. The glucose component cannot be converted with conventional yeast used for grain sugar fermentation.

## Experimental Plant Evaluations

Based on results of bench-scale testing, a low-temperature acid hydrolysis experimental facility was designed and built (Barrier et al. 1985a). Construction of the sugar facility began in November 1983 and the distillation facility in April 1984. The acid hydrolysis experimental plant is housed in an 18 × 24 × 9-m insulated metal building. The fermentation vessels and distillation column are in an adjacent building. Sugar solutions are pumped from the hydrolysis plant to the fermentation vessels.

All process piping vessels and reactors in contact with corrosive concentration of sulfuric acid are made of vinyl ester resin fiberglass-reinforced plastic (FRP). The dryer is made of carbon steel and lined with Kynar. Conveyor belts are made of acid-resistant materials. Mild steel agitator shafts are coated with Kynar or Teflon. Heat exchangers are made with CPVC pipe shells and Carpenter 20 stainless steel coils. Pumps are made with

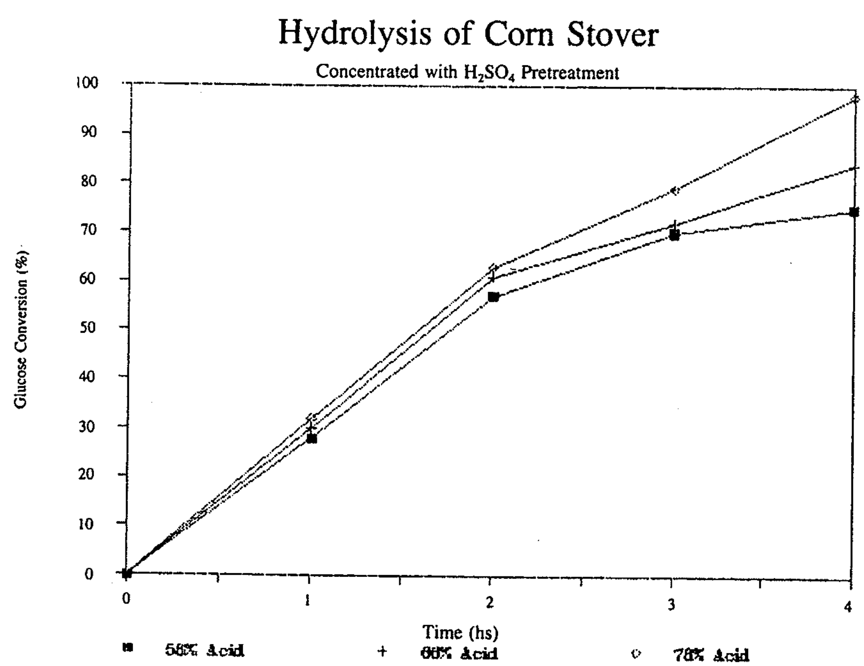


**Figure 2.** Glucose conversion vs. time for different acid pretreatment concentrations: ■, 58%; +, 66%; ◇, 78%.

nonmetallic compounds, Teflon linings, or Carpenter 20 stainless steel. The two filter press units have plates made of polypropylene.

### *Experimental Plant Process Tests*

Five experimental plant tests have been conducted to evaluate processing steps and conversion efficiencies for producing reducing sugars from corn stover (Barrier et al. 1985b, 1986). Conversion efficiencies for these plant tests have exceeded laboratory yield. Overall hemicellulose and cellulose conversion exceeded 90%.

The July 1984 test required some modification of the process. The leaching sequence was deleted because the material to fabricate the leaching screen had not been received. Also, the vacuum dryer was unable to maintain the stover/acid mixture at 65 °C, thus the 80% acid concentration required for cellulose hydrolysis was not attained. Results from this run showed a 74% conversion of hemicellulose to xylose and 36% conversion of cellulose to glucose.

The September 1984 test was conducted to assess the performance of a leaching screen in the hemicellulose reactor and to determine overall conversion efficiency in the first stage of the process. Results of the run showed adequate leaching of liquid from the stover with the new screen. The hemicellulose conversion efficiency was 80%.

The process was again modified during the November 1984 tests. In that test, first-stage residue from the hemicellulose reactor was conveyed directly to the vacuum dryer, bypassing the prehydrolysis step. The stover was dried to 33% solids and conveyed to the cellulose reactor. In the cellulose reactor, the stover was mixed with 85% sulfuric acid to disrupt the cellulose crystalline structure. After 30 min, water was charged to the reactor to give a final acid concentration of 30%. The reactor contents were heated to 100 °C and maintained at that temperature for 4 h. The lignin was filtered off and the glucose/acid mixture was added to the xylose product from the hemicellulose conversion step.

The basic process concepts were proven during the November test. Conversion efficiencies for the corn stover hemicellulose and cellulose fractions were 97 and 90%, respectively.

Another process evaluation test was conducted in June 1985. All process steps performed satisfactorily, and conversion efficiencies for the hemicellulose and cellulose components of the corn stover feedstock averaged 98 and 92%, respectively.

Based on these tests, several process areas are being developed and improved in plant and laboratory studies. The plant will be modified to incorporate technology that will allow recovery and recycling of sulfuric acid from the product stream. Other improvements to simplify and improve processing and materials handling will also be made.

## Integrated Biomass Refinery System

In addition to ethanol production from corn stover, production of multiple products from other agricultural residues and forage crops, such as alfalfa, is being studied at TVA. An important benefit of forage crops is that many can be grown on potentially erodible soils. This slows soil erosion and increases soil tilth. Results of these preliminary studies indicate that the experimental plant can be modified so that products such as protein and methane can be efficiently produced.

Several processes can be used to extract protein from biomass sources such as forage crops. These processes may increase crop value. Based on research studies (Dale 1983),

the protein extraction process most compatible with the TVA experimental facility involves leaf and stem separation. The leaf fraction from alfalfa, for example, is high in xanthophyll and protein (about 25% each) and has a low fiber content. High-protein forage crops such as alfalfa, kobe lispedeza, or rye grass would be cut, dried, and harvested in the field using conventional hay harvesting equipment and transported to the processing facility for grinding, to lengths of about 3 mm, and leaf and stem separation using air classification. Lignin is the unreacted fraction of the feedstock following hydrolysis. Lignin can be burned as a boiler fuel. It has a heating value of about 5270 kcal/kg, which is comparable to that of subbituminous coal. The corn stover is about 25% lignin on a dry weight basis. Many forage crops have similar lignin concentrations. Other products, such as surfactants and adhesives, can be made from lignin. Research is being conducted to evaluate processing requirements and marketability of such products.

Stillage is the effluent from the distillation process. Stillage can be used to produce several products, including methane. Preliminary research has shown that 30 L of biogas containing 60% methane is produced from a liter of corn stover stillage. For each liter of ethanol produced, 10 L of stillage is produced.

### *Alternative Feedstock Evaluations*

Ten feedstocks have been evaluated in bench-scale studies to determine material handling qualities, processing requirements, and conversion efficiencies. The feedstocks evaluated include fescue, alfalfa (from Colorado), alfalfa (from the Tennessee Valley), grain sorghum residue, coastal bermuda, red clover, kobe lespedeza, winter rape residue, sugar cane bagasse, rice hulls, and corn hulls. Each feedstock was analyzed for lignin hemicellulose and cellulose content.

No processing difficulties were encountered during acid hydrolysis of the 10 feedstocks. Preliminary conversion efficiencies for all 10 feedstocks were similar to results obtained using corn stover. The conversion efficiency of rice hulls in the first-stage hydrolysis was 40%, but after cellulose hydrolysis, total hemicellulose conversion was 95%. The low first-stage hydrolysis may be due to the high lignin content (43.5%), which requires more severe acid hydrolysis conditions to convert the hemicellulose.

## Summary

Two years of experimental facility testing has demonstrated that the concept of concentrated acid hydrolysis is workable. Conversion efficiencies of hemicellulose and cellulose to sugars have exceeded 90% in tests with corn stover. Laboratory testing of alternative feedstocks gave similar results. Economics of the acid hydrolysis process are being improved by combining processing steps and improving process conditions. Acid recovery research is being conducted to decrease acid consumption in the process.

Development of an integrated biomass refinery system for converting lignocellulosic feedstocks to feeds, fuels, and chemicals is progressing. Integrated system processing requirements are being identified, and experimental plant modifications are being evaluated.

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